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VAPOR PRESSURE
OF CYCLOHEXYL METHYLPHOSPHONOFLUORIDATE (GF)

David E. Tevault
James H. Buchanan
Leonard C. Buettner

RESEARCH AND TECHNOLOGY DIRECTORATE

Kathy L. Matson

GEO-CENTERS

GEO-CENTERS, INC.
GUNPOWDER, MD 21010-0068

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ABERDEEN PROVING GROUND, MD 21010-5424

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14. ABSTRACT

The vapor pressure of cyclohexyl methylphosphonofluoridate (also known as cyclosarin or GF) has been measured between 0 and 40 °C using vapor saturation methodology. The current data indicate that the volatility of GF is higher than projected based on data previously measured by ca. 20% at 25 °C and more than twice as high at -10 °C.

15. SUBJECT TERMS

Cyclohexyl methylphosphonofluoridate	Naphthalene	GF
Vapor pressure	Cyclosarin	
Chemical agent	Volatility	

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VAPOR PRESSURE
OF CYCLOHEXYL METHYLPHOSPHONOFLUORIDATE (GF)

1.   INTRODUCTION

The vapor pressure of GF has been measured previously using differential thermal analysis (DTA) between 66 and 168 °C (1) and effusion between 14 and 30 °C (2). A correlation based on those data has been published (3).

The vapor pressure of a large number of CW agents has been measured in the ambient temperature range recently using a modified ASTM vapor saturation method (4-5 and unpublished data*). The current GF vapor pressure measurements have been performed using vapor saturation and span the temperature range of 0 to 40 °C.

2.   EXPERIMENTAL PROCEDURES

The quantitative data reported herein were measured using Hewlett-Packard model 5890 gas chromatograph (GC) equipped with a flame ionization detector (FID). Nitrogen was used as the GC carrier [8 standard cubic centimeters per minute (sccm)] and detector make-up (22 sccm) gas. Combustion gases were air (400 sccm) and hydrogen (32 sccm). The GC column (Restek Corp., Bellefonte, PA), a 15-m x 0.53-mm i.d. fused silica column with 1.0-μm RTx-5 (95% polydimethylsiloxane, 5% phenylmethylsiloxane) film, was programmed from 50 °C to 170 °C at a rate of 20 °C/min. Using the instrumentation and operating conditions described, GF eluted at 4.0 min, representing a GC column temperature of 130 °C.

All calibrations were performed by adding an accurately measured amount of analyte to the appropriate solvent and measuring the resulting GC peak areas. The saturation method for measuring vapor pressure of chemical warfare (CW) agents has been described in detail in prior publications from our laboratory (4-5).

The saturator methodology has been slightly altered in the present work owing to the relatively high vapor pressure of GF compared to the majority of compounds investigated previously. The modification used in the GF measurements reported here used a sample loop of approximately 1 cc volume. The volume of sample loop was calibrated using the known vapor pressure of naphthalene. The sample loop volume was then used to calculate the vapor pressure of GF.

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A second independent GF vapor pressure determination was performed to verify the gas loop data. In that work, a different HP 5890 GC-FID system was calibrated as before using liquid injections of dissolved GF. In the latter work, saturator effluent was collected by drawing a controlled volume of GF vapor in carrier gas directly into a tenax sorbent tube and immediately desorbing the collected vapors into the GC as before (4-5 and unpublished data*).

GF (lot 93-0034-121.3) was found to be 99% pure by GC/MS-EI analysis and was used without further purification. High-purity naphthalene (scintillation grade, 99+%) was purchased from Aldrich Chemical Company, Inc. (Milwaukee, WI) and used without further purification. Calibration curves relating analyte mass and GC area were determined prior to measuring saturator data for each compound using standard methodology. The vapor pressure of GF was determined as before using equation 1.

$$P_{chem} = P_{ambient} \bullet (N_{chem})/(N_{chem} + N_{N2})/y_{chem} \tag{1}$$

where:

P_{chem} = vapor pressure of the analyte (naphthalene or GF)
$P_{ambient}$ = ambient pressure at the time of the measurement
N_{chem} = number of moles of analyte (naphthalene or GF)
N_{N2} = number of moles of nitrogen carrier gas
y_{chem} = analyte purity

The number of moles of carrier gas (nitrogen), and thus the volume of the sample loop, was determined initially using naphthalene since its vapor pressure is well known and the other parameters in equation 1 could be determined experimentally. For the work reported here, the denominator of equation 1 can be very accurately approximated by neglecting the analyte owing to its low partial pressure compared to that of the carrier gas. N_{chem} was determined for both analytes from the GC measurement using the previously determined analyte mass vs. GC area calibration. GF vapor pressure was determined using the sample loop volume determined from the naphthalene data.

To confirm that the experimental system was operating under equilibrium conditions, the saturator flow rate was varied between 25 and 50 sccm. No effect was observed on measured data by changing the carrier flow rate.

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Data acquisition was controlled and recorded using National Instruments LabView® software and interfaces (SCXI 1001 chassis equipped with various 1320-series modules). Controlled parameters included the temperature of the saturator bath and saturator flow rate. Measured data included ambient pressure and GC area. All of the data were captured and stored by the control program.

3.   RESULTS AND DISCUSSION

In previous work from our laboratory, the vapor pressure of naphthalene was measured using the sorbent tube method . The results of those measurements agree well with previous literature data (6-9) and are listed in Table 1 and plotted in Figure 1. The difference between our measurements and the literature naphthalene data was less than 3.5% on average and validate the present saturator methodology.

Table 1. Naphthalene Data Measured Using the Saturator Method.

Temperature (°C)	Vapor Pressure (Pa)
-9.8	0.228
0.1	0.751
9.9	2.40
20.3	6.99
30	16.4

Belkin has reported GF vapor pressure data between 66 and 168 °C measured using DTA (1). Neale reported GF vapor pressure data between 14 and 30 °C measured using Knudsen effusion (2). Table 2 lists the GF data measured in the present work using the gas sample loop method, and Table 3 lists the GF data measured in the present work using the sorbent tube sampling method. Figure 2 shows a plot of the current GF vapor pressure data measured using the gas sample loop method superimposed on previous data along with a new Antoine fit based on the saturator and DTA data only. The new Antoine coefficients are listed in Figure 2. Figure 3 is a magnified plot of the saturator data and demonstrates the agreement between the two methods.

The Antoine coefficients in the literature (3), based on previously measured data above 15 °C, were used to project vapor pressures in the range of the current data and were found to underpredict the saturator data by as much as a factor of 2. As shown in Figure 2, the data points generated using effusion are significantly lower than observed by the vapor saturation method, and those points were not used to derive the Antoine coefficients shown in Figure 2. The average difference between the correlation value and observed value for data plotted in Figure 2 is 4.1%, and the vast majority of that error is contributed by the low end DTA data. While a similar

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argument can be made in order to correlate the DTA and effusion data, the average error in that case is greater than 6%, possibly indicating that the effusion data stress the DTA data more than the saturator data, casting further suspicion that the effusion data are in error.

The average difference between saturator data measured using the gas sample loop method and correlation prediction is 0.2%, indicating highly precise methodology. To demonstrate the accuracy of the saturator method, a second independent GF vapor pressure determination was performed using a method more closely related to previous work from our Laboratory. In that work, a sorbent tube was teed directly into the saturator effluent line, and a controlled volume of sample was drawn into the tube and immediately desorbed into the GC-FID apparatus. The results of those experiments, along with the gas loop data, are shown in Figure 3. As seen in Figure 3, the sorbent tube data are in excellent agreement with the values measured by the gas loop method and predicted by the Antoine correlation, with an average error between all saturator data and correlation amounting to 1.3%, half of which is contributed by the sorbent tube data point at 15 °C.

Vapor pressure data reported previously for GF are listed in Table 4, and predictions based on the old and new Antoine coefficients are presented in Table 5. Table 5 demonstrates that the projected GF vapor pressure based on correlations to the prior data diverges from the current values as the temperature decreases and underestimates the GF vapor pressure by nearly a factor of 1.65 within the range of measured data (ca. 0 °C) and in excess of a factor of two at - 10 °C.

Table 2. Vapor Pressure Measured in this Work for GF Between 0 and 40 °C by Vapor Saturation Using a Calibrated 1.29-cc GC Sample Loop.

Temperature (°C)	Measured Vapor Pressure (Pa)
0.3	1.19
5.3	1.94
10.2	3.11
15.2	4.87
20.2	7.47
25.2	11.3
30.2	16.9
35.2	24.8
40.2	36.0

Table 3. Vapor Pressure Measured in this Work for GF Between 5 and 18 °C
by Vapor Saturation Using the Sorbent Tube Sampling Method.

Temperature (°C)	Measured Vapor Pressure (Pa)
5.0	1.95
9.8	3.09
15.0	4.64
18.0	5.90

Table 4. Prior Vapor Pressure Data for GF.

T (°K)	VP (Pa)
From Belkin (DTA)	
167.5	17785
156	11746
145	8359
138.5	63723
123	3253
115.5	2453
109	1653
96	1093
85.5	733
78.5	500
66	207
54	86.7
From Neale (Knudsen Effusion)	
30.3	14.0
25.3	9.12
21.1	6.92
18.2	4.95
14.3	3.47

Table 5. Vapor Pressure of GF Between - 10 and 40 °C Predicted Using New and Previously Published Antoine Coefficients and Heat of Vaporization. Entries in bold are extrapolated beyond the range of measured data.

T (°C)	$VP_{calculated}$ (Pa) (New Antoine Equation)	$VP_{calculated}$ (Pa) (Old Antoine Equation)	ΔH_{vap} (kcal/mol)
-10	**0.401**	**0.195**	**15.23**
-8	**0.500**	**0.255**	**15.17**
-6	**0.619**	**0.330**	**15.12**
-4	**0.765**	**0.426**	**15.07**
-2	**0.942**	**0.545**	**15.02**
0	1.15	0.694	14.96
2	1.41	0.880	14.92
4	1.72	1.11	14.87
6	2.08	1.39	14.82
8	2.52	1.73	14.77
10	3.03	2.15	14.73
12	3.64	2.65	14.68
14	4.36	3.26	14.64
16	5.21	3.99	14.59
18	6.20	4.86	14.55
20	7.36	5.90	14.51
22	8.71	7.13	14.47
24	10.3	8.58	14.43
26	12.1	10.3	14.39
28	14.2	12.3	14.35
30	16.6	14.7	14.31
32	19.4	17.4	14.27
34	22.6	20.6	14.24
36	26.3	24.2	14.20
38	30.5	28.5	14.16
40	35.4	33.4	14.13

The following is a list of Antoine coefficients in terms of Torr pressure units according to Equation 2.

$$\log VP \text{ (Torr)} = a - b/(c + t) \tag{2}$$

$$a = 7.684$$

$$b = 2166.74$$

$$c = 222.4$$

$$t = {}^\circ C$$

Conversion between the Antoine equation in Pascal units shown in Figure 2 and Torr units shown immediately above is performed as follows:

$$a_{Pa} = a_{Torr} \bullet \ln (10) + \ln (101325/760) = 2.303 \bullet a_{Torr} + 4.893$$

$$b_{Pa} = b_{Torr} \bullet \ln (10) = 2.303 \bullet b_{Torr}$$

$$c_{Pa} = c_{Torr} - 273.16$$

4.   CONCLUSIONS

Accurate vapor pressure data for threat agents is required operationally for estimating persistence as well as downwind concentration profiles. The data are also required in the laboratory in order to accurately and predictably generate known concentrations for a variety of developmental applications, including detector performance and calibration, toxicology studies, and decontamination efficacy. The current work has revealed a significant underestimation of the volatility of one of the classical CW agents, which had not been accurately measured in the ambient temperature range prior to this work. We believe that the vapor saturation method is capable of generating accurate vapor pressure data for CW agents with volatility as low as that of VX, however, these are extremely difficult measurements, and little independent validation is available.
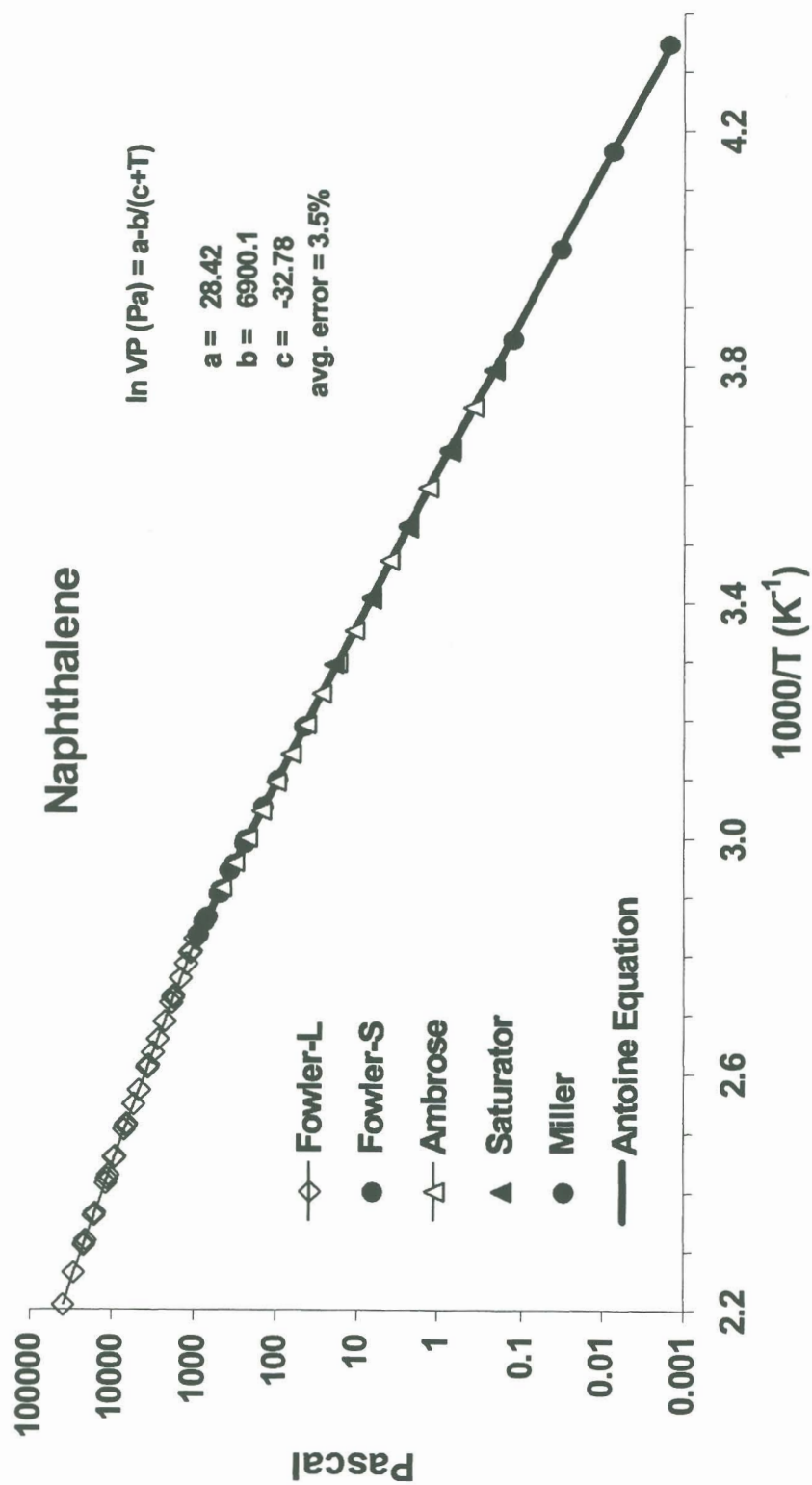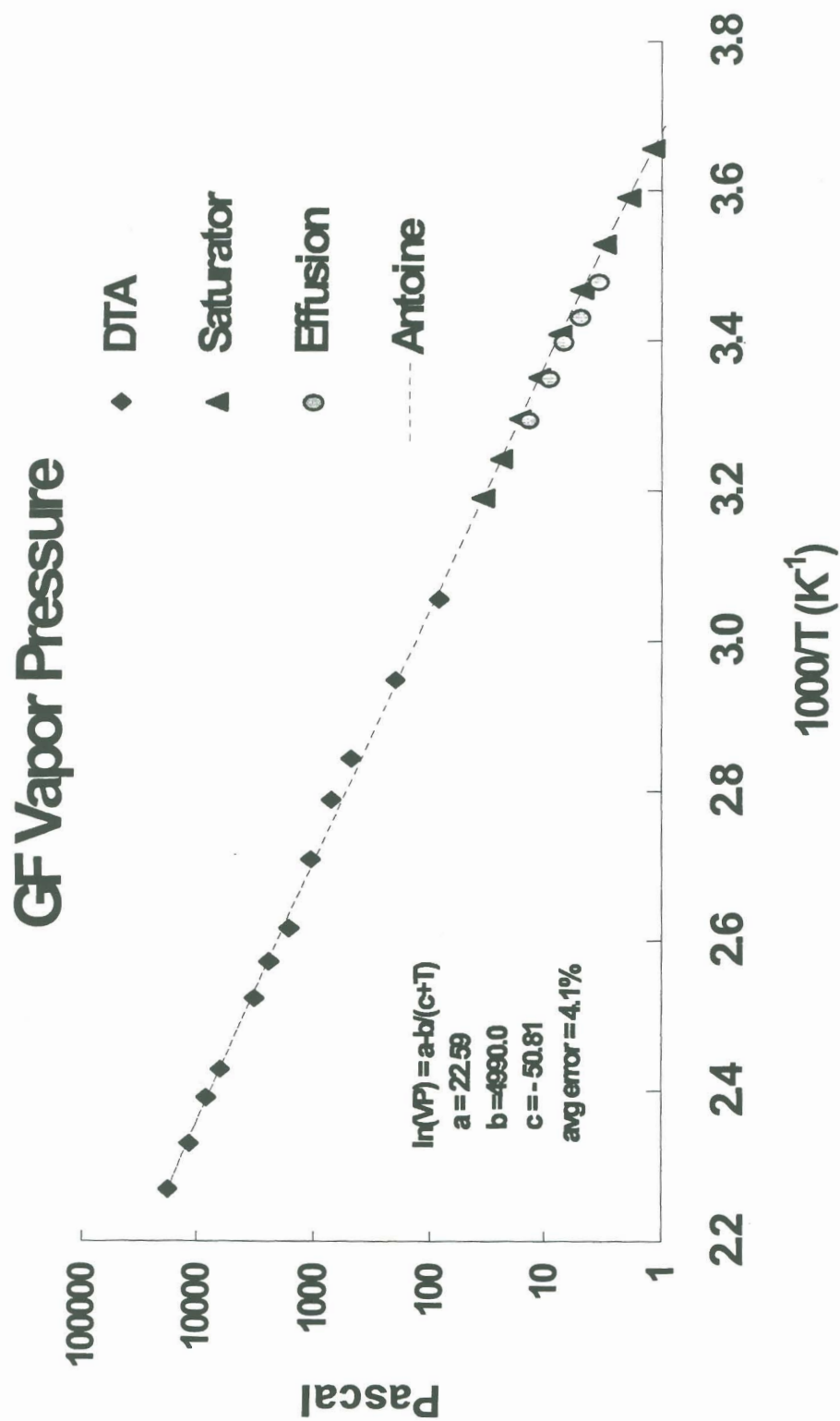
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Figure 1. Vapor Pressure and Antoine Fit for Naphthalene. Break in curve denotes the melting point. Average error represents the difference between saturator data and Antoine equation only.
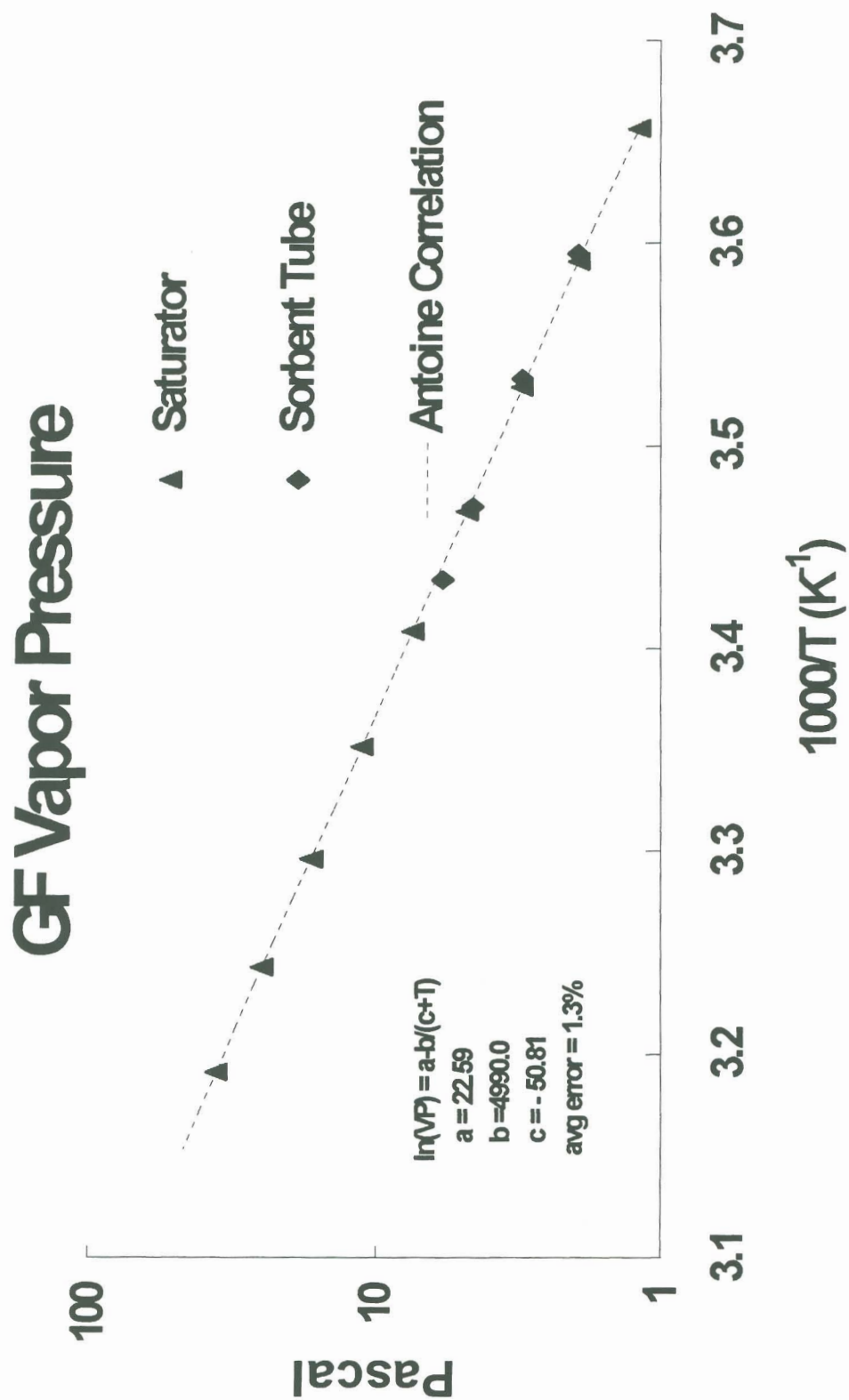
Figure 2. Vapor Pressure Plot of GF. New Antoine equation based on DTA and saturator data only. Average error denotes differences between those data and Antoine predictions.

Figure 3. Vapor Pressure Plot of GF Measured in this Work Using Vapor Saturation.

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